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This report is a summary of the air quyear 1979. This annual summary is part of summarized include ozone (O ₃), sulfur diototal hydrocarbons (THC), methane (CH ₄), (CO), air temperature, relative humidity, wat the NRL air monitoring station are inter-	ality data measured a continuing series is kide (SO ₂), nitric ox , non-methane hydro ind direction, and w	nitiated in 1975. The variables kide (NO, nitrogen dioxide (NO ₂), ocarbons (RHC), carbon monoxide ind speed. The instruments in use

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20. Abstract (Continued)

coupled to a magnetic tape recorder. The data input is for one month on a tape which is subsequently analyzed by the NRL air computer program and results in a monthly computer printout of the essential air quality data. Each of the monthly computer printouts is then analyzed and a digest of the information obtained is reported as the annual summary. Included in the report is some background information thought necessary in understanding the data. Finally, a brief description of the odor nuisance problem at NRL is described.

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CONTENTS

INT	RODUC	CTIC	N	•	•	•	•	•	•	1
BAC	KGROL	JND	•	•		•	•	•		1
GENE	ERAL	INF	ORM	ATIO	N	•	•	•	•	1
AIR	QUAL	YT1.	DA.	TA A	ND RI	ESUL'	TS	•		3
					ents	•		•		3
					Data	1	•	•	•	5
	Air	Qua	lity	/ Da	ta	•	•	•	•	7
AIR	QUAL	YT I.	STA	ANDAF	RDS		•	•		31
ODOR	NUI	SAN	CE A	AT NE	RL	•		•	•	32
FUTU	IRE P	LAN	S	•	•	•	•		,	34
SUMM	IARY			•	•		•		•	34
REFE	RENC	ES			•					35

THE 1979 NRL AIR QUALITY DATA

INTRODUCTION

This report is the fifth in a continuing series of yearly summaries of the air quality data measured at NRL (1,2,3,4). The present review includes the air quality data for the calendar year 1979. The variables measured and recorded during this time were ozone (0_3) , sulfur dioxide (SO_2) , nitric oxide (NO), nitrogen dioxide (NO_2) , total hydrocarbons (THC), methane (CH_4) , non-methane hydrocarbons (RHC), carbon monoxide (CO), air temperature, relative humidity, wind direction, and wind speed.

The purpose of the report is to characterize, interpret, and summarize the large amount of the air quality data generated over the one-year period.

BACKGROUND

The NRL air monitoring station is located in Building 207, Room 409. Details in the housing and instruments in use have been reported in a previous publication (5). Some new additional instruments in use at the NRL air monitoring station during the calendar year 1979 included a continuous nitrogen oxides (NO_x) analyzer (based on the reaction between nitric oxide (NO) and ozone which produces light energy at a given wavelength). Any nitrogen dioxide (NO_2) in the ambient air is converted to NO, and the total NO, as NO_2 plus NO, is the total oxides of nitrogen, $NO_{\rm X}$. Electronic subtraction of NO from $N0_x$ yields $N0_2$ in ppmv), an air temperature system using a radiation shielded thermocouple, and a continuous relative humidity monitor using the hair hygrometer principle. The instruments in use are interfaced to a data acquisiton system which is, in turn, coupled to a magnetic tape recorder. The input on the magnetic tape is in 5-minute average electrical voltages. A tape is run continuously for one month and the data is retrived, via the air quality computer program with a computer printout of the essential air quality data (6). The air quality data from the monthly computer printouts were used to extract the main body of information contained in this report.

GENERAL INFORMATION

At any given time, there are thousands of substances present in the ambient air. These materials enter the atmosphere from natural

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sources (dust storms, forest fires, lightning, sea salt spray, vegetation, and volcanos), human activity (agricultural practices, animal husbandry, commercial establishments, highway and roadway construction, industrial and manufacturing operations, institutions, solid and liquid waste disposal, and transportation systems). tropospheric-stratospheric exchange, and extra-terrestrial entry of cosmic debris into the earth's atmosphere. From these sources, materials injected into the atmosphere include gases, liquids, and solids. A few of these substances form the natural composition of the atmosphere as it has evolved up to the present time, some are inert, others reactive or act as catalysts; while, for a great number, much remains to be understood. A select few have been recognized as interfering with human health and welfare, i.e., the air pollutants. An air pollutant may be defined as a chemical substance, usually a product of human activity, that has a negative effect on human wellbeing, and whose deleterious effects are above a given concentration (this concentration may be zero, or equal to the background value).

Air pollutants, singly or in combination with other substances, cause, or accelerate, acid rain (below pH 5.5), building grime, deteriorating climatic changes, fabric damage, human and animal sickness, metal corrosion, vegetation damage, and visibility degradation. In addition, the effects of an air pollutant may be immediate (acute) or long-term (chronic). Acute response may be discerned in minutes, hours, or days, while chronic symptoms may be revealed in months, years, or even longer periods of time. For humans, the effects of air pollutants, directly or indirectly, are associated with asthma, cancer, cardiovascular problems, chronic bronchitis, eye irritation, odornuisance, and respiratory diseases.

Some of the recognized air pollutants that cause such concern include asbestos, beryllium, carbon monoxide, lead, mercury, nitrogen dioxide, ozone, particulate matter, and sulfur dioxide. Other air pollutants include carbon dioxide, Freons, nitric acid, organic and inorganic sulfates, polynuclear hydrocarbons, sulfuric acid, as well as a number of inorganic and organic halogens, nitrogen, oxygen, and sulfur compounds, which are recognized as air pollutants, or are precursors or promoters of air pollutants. The influence of these substances may vary from curbside, fenceline, street, city, metropolitan area, region, national, international, or global, and, with respect to human response, may vary from a single individual to the entire earth's population, or affect areas where one lives, plays, or works.

In urban communities, like the metropolitan Washington area, the main sources of air pollutants are the result of human activity (anthropogenic sources) and include emissions from air traffic, commercial establishments (dry cleaning plants, gasoline stations,

restaurants, etc.), electric power plants, heating plants, incinerators, institutions, light industry, motor vehicles, residential home heating units, and sewage treatment plants. These emission sources may be further described as: area-line-source, combustion-noncombustion, continuous-intermittent, elevated-ground, gas-liquid-solid, inorganic-organic, and/or urban-suburban-local. In any case, the total quantity of air pollutants combined is significant and may well be several thousand tons per day.

The lifetimes of the air pollutants, or any trace substances present in the atmosphere, depend on the sequence emission-transportreceptor and may last from a few minutes to several years, or longer. Once an air pollutant is emitted into the atmosphere, or is formed there, it is diluted and dispersed by horizontal advection (wind) and/or vertical convection. Their subsequent fate is determined by meterological conditions and reactivity (reaction rate). Scavenging mechanisms such as precipatation, clouds, and dry deposition (impingement on surfaces) remove most of the air pollutants from the atmosphere or transport them to another area. Some air pollutants are slow reacting and reactions may occur far from their source. Other air pollutants are highly reactive and may form other more potent air pollutants. Still other substances are inert, or are ineffectually removed from the atmosphere by scavenging mechanisms, and may persist in the atmosphere for long periods of time, Therefore, non-reactive substances will have time to build up their background concentrations to as yet unforeseen effects.

The sequence, emission-transport-receptor, is also a neverending, overlapping cycle. Superimposed on this sequence are air pollutants from other metropolitan areas. Exchange of air pollutants may occur within Washington, D. C.-Baltimore, Maryland; Washington, D. C.-Richmond, Virginia; and with other areas further away. Consequently, the concentrations measured and recorded at the NRL air monitoring station are from a combination of sources: natural, local human activity (fresh), and from long distance human activity (aged). However, for most practical purposes, the emission sources from local human activities will be considered the most influential in biasing the air quality data.

AIR QUALITY DATA AND RESULTS

Valid Measurements

Table I lists the number and percent of valid hourly measurements of each variable measured and recorded during the calendar year 1979.

Table 1
Valid Number and Percent of Measured and Recorded Air Quality Data

Variable	Number of Hours	Percent of Hours*
03	7376	84.2
SO ₂	7307	83.4
THC	6647	75.9
CH ₄	6647	75.9
RHC	5860	66.9
co	6647	75.9
NO	5972	68.2
NO ₂	5972	68.2
wind speed	7521	88.9
wind direction	7521	88.9
air temperature	7541	85.9
relative humidity	7301	83.4

Instrument downtimes were due to calibration procedures, maintenace and repair work, and electrical glitches. In addition, the number of hourly observations were decreased because the magnetic tape recorder was started on the first working day of the month and turned off on the last working day of the month, or as close as possible to those days. Even so, the percentages listed in the table are high

enough to give, for each variable, a reliable estimate of representative values for any time-averaging period of interest.

Percentages less than 49% would be considered a poor representation of the data, 50%-59% would be considered fair, 60%-74% good, and above 75% excellent. Obtaining higher percentages would require backup systems for most of the instruments in use.

Meteorological Data

Table 2 lists the percent occurrence of each of the sixteen wind directions measured and recorded during the calendar year 1979. Also included in the table is the average wind speed for each of the wind directions.

	Table 2					
	Percent Occurrence of Each Wind Direction and Corresponding Average Wind Speed					
Wind Direction	% Occurrence	Average Wind Speed (mph)				
NNW	13.6	11.0				
S	12.9	6.7				
NNE	9.5	7.9				
N	9.1	8.4				
SSW	9.1	6.9				
SW	9.1	8.1				
SSE	8.3	8.2				
NW	7.2	10.0				
NE	4.9	7.5				
WSW	3.6	7.1				
\$E	2.8	8.3				
WNW	2.6	9.1				
ENE	2.3	8.8				
W	1.7	8.2				
Ε	1.7	8.9				
ESE	1.6	9.9				

As shown in the table, the prevailing wind direction was NNW. This wind direction lies in the Virginia sector, with respect to the Laboratory, and directly in line with the Washington National Airport (2 miles). The airport accommodates about 1000 operations per day. Other nearby reference points, and possible emission sources, are

the Pentagon (3-1/2 miles), and the approaches, on the Virginia side, to the George Mason Memorial, Center Highway, and Rochambeau Memorial bridges.

The second most prevailing wind direction during 1979 was south. In this direction lie the Blue Plains Sewage Treatment Plant (NRL's neighbor) and the Wilson Bridge (2 miles); the bridge is a part of the Washington Beltway-Route 495 (and 95). The traffic on the bridge is approximately 103,000 motor vehicles per workday. Also, from this wind direction, the air traffic (landings and takeoffs) is about 500 operations per day.

The third most prevailing wind direction during the year was NNE. In this direction, with respect to the Laboratory, lies most of the downtown section of the District of Columbia. Reference points for this wind direction are the Washington Navy Yard (3-1/2 miles) and the U. S. Capitol (4-1/2 miles). A major emission source from this wind direction is the Benning Road electric power plant (5-3/4 miles). Another major emission source, the Buzzard Point electric power plant, lies midway between the N and NNE wind direction.

Fortunately, for the Laboratory, some nearby major emission sources are located in the least prevailing wind directions. For example, to the west, across the Potomac River, on the Virginia side, is located a coal-fired electric power plant (1 mile) which burns about one million tons of coal a year. In the east is the Anacostia Freeway, Route 295, with about 53,000 motor vehicles per workday. Of course, what is favorable for the Laboratory is not so favorable for some other areas.

Within the Laboratory grounds is located the NRL heating plant (SSW of the air monitoring station) which, during 1979, consumed 3,859,275 gallons of fueloil (mostly #6). The major air pollutants for this type of emission sources are particulate matter, sulfur dioxide, and nitrogen oxides, with lesser amounts of other pollutants being emitted such as hydrocarbons and carbon monoxide. Other emission sources within the Laboratory may be considered insignificant except on a local level. One may, however, consider no source as insignificant since it is the combined output of all emission sources that determines the air quality of a given area.

Another important meteorological condition that influences pollutant concentrations is surface-based temperature inversions; also called nighttime or radiation inversions. This is measured routinely at the NRL air monitoring station and is based on an indirect method developed at the Laboratory (7). This type of inversion is indicated by a temperature increase in altitude from the ground surface up to a given height; depending on the strength of the inversion. With corresponding low wind speeds, a usual condition at night, the pollutants

are trapped within the inversion layer since horizontal and vertical dispersion is limited. Generally, this type of inversion is initiated in the late evening or early morning hours, peaks in the mid-morning hours, and decays in the early afternoon hours. After the surface-based temperature inversion is dissipated, the pollutants are diluted and dispersed with fresh incoming air.

In addition to the daily occurrence of surface-based temperature inversions, there is another type of inversion that results in high pollutant concentrations. This condition is known as the subsidence temperature inversion and occurs aloft at a higher layer of the troposphere. The subsidence inversion results from the sinking of air at great altitudes above a high pressure region. As this air descends, it gains heat and forms a deep warm layer that overlies the cooler air beneath it. Consequently, high pressure systems are related to subsidence temperature inversions. When a high pressure system hovers over an area, or moves slowly (stagnating anti-cyclone), vertical motion is diminished and pollutant concentration build-up is enhanced. In fact, these are the conditions when most severe air pollution episodes occur.

Air Quality Data

The actual air pollutants for which air quality standards have been issued by the federal government, and which were measured and recorded at the NRL air monitoring station during the calendar year 1979, included carbon monoxide (CO), nitrogen dioxide (NO2), nonmethane hydrocarbons (RHC), ozone (O3), and sulfur dioxide (SO2). In addition, air quality data were also collected for methane (CH4), nitric oxide (NO), and total hydrocarbons (THC). These gases, although not presently considered as air pollutants, serve to identify emission sources, enter into chemical reactions in the atmosphere, relate concentration fluctuations to corresponding meteorological conditions, and/or establish concentration profiles typical of gaseous behavior in the atmosphere.

For each gas, a table of air quality data has been constructed listing for each month, in ppmv, the monthly average, the maximum concentrations for the three time-averaging periods of interest, i.e., 5 minutes, 1-hour, and 24-hours. The table for CO includes the 8-hour maximum concentration, and for THC, CH_4 , and RHC the 3-hour maximum concentration that occurred in the period corresponding to the morning rush hour traffic (6 a.m. - 9 a.m.). At the bottom of each table, the representative yearly average is shown. This information is listed in Tables 3 - 10.

	<u> </u>	Table 3		
**************************************	Air Quali	ty Data for 0_3 i		
Month	Monthly	5-min	C _{max}	24-hr
MOTICA	Average		l-hr	
January	0.006	0.015	0.013	0.009
February	0.009	0.039	0.037	0.019
March	0.006	0.021	0.021	0.011
April	0.032	0.387	0.355	0.047
May	0.027	0.159	0.075	0.048
June	0.032	0.101	0.096	0.051
July	0.034	0.130	0.121	0.052
August	0.034	0.141	0.132	0.053
September	0.023	0.145	0.134	0.038
October	0.016	0.082	0.075	0.032
November	0.017	0.342	0.085	0.040
December	0.013	0.046	0.044	0.027
representat	ive yearly ave	rage = 0.021 ppm	V	

		Table 4		
	Air Quali	ty Data for SO ₂	in ppmv	
	Monthly		max	
Month	Average	5-min	1-hr	24-hr
January	0.028	0.300	0.206	0.046
February	0.019	0.184	0.074	0.035
March	0.026	0.163	0.089	0.039
April	0.017	0.169	0.089	0.034
May	0.015	0.163	0.072	0.032
June	0.013	0.320	0.139	0.027
July	0.013	0.269	0.107	0.022
August	0.012	0.269	0.093	0.021
September	0.013	0.269	0.084	0.031
October	0.015	0.322	0.097	0.031
November	0.018	0.282	0.077	0.031
December	0.022	0.384	0.173	0.053
representat	ive yearly ave	rage = 0.018 ppm	nv	

Table 5						
	Air Quali	ty Data for NO i	n ppmv			
	Monthly		Cmax			
Month	Average	5-min	l-hr	24-hr		
January	0.025	0.435	0.377	0.078		
February	0.028	0.425	0.327	0.101		
March	0.031	0.485	0.422	0.128		
April	0.008	0.181	0.153	0.028		
May	0.009	0.424	0.362	0.066		
June			••			
July	0.008	0.260	0.113	0.029		
August	0.013	0.233	0.183	0.042		
September	0.024	0.384	0.339	0.104		
October	0.034	0.473	0.375	0.122		
November	0.054	0.485	0.425	0.221		
December						
representat	ive yearly ave	rage = 0.023 ppm	1V			

Table 6					
	Air Quali	ty Data for NO ₂	in ppmv		
	Monthly		C max		
Month	Average	5-min	l-hr	24-hr	
January	0.024	0.050	0.040	0.037	
February	0.028	0.155	0.122	0.055	
March	0.026	0.101	0.085	0.052	
April	0.021	0.140	0.119	0.058	
May	0.010	0.070	0.065	0.032	
June	**	**			
July	0.035	0.127	0.118	0.063	
August	0.019	0.082	0.066	0.030	
September	0.022	0.130	0.095	0.047	
October	0.023	0.151	0.128	0.070	
November	0.033	0.256	0.191	0.101	
December					
representat	ive yearly aver	age = 0.024 ppm	1V		

	A:- 0:	Table	•		
		ality Data	for CO in ppr C_		
Month	Monthly Average	5-min	C _{ma}	8-hr	24-hr
January	1.42	7.53	5.95	3.42	2.09
February	1.67	10.76	7.16	5.49	3.53
March	1.80	29.27	23.31	8.48	3.66
April	1.75	23.27	23.04	12.41	2.15
May	1.08	26.97	6.21	2.79	1.24
June	0.98	2.95	1.91	1.57	1.16
July	1.59	18.09	6.71	6.69	3.99
August	0.96	16.67	2.41	1.24	1.04
September	1.26	9.79	7.20	4.58	2.79
October	1.63	11.39	8.27	5.84	3.33
November					
December	1.99	12.35	6.78	5.35	4.00
representa	tive yearly a		47 ppmv		

		Table			
	Air Qu	ality Data	for THC in pr	OMV	·
	Monthly			nax	·
Month	Average	5-min	i-hr	3-hr	24-hr
January	2.19	12.32	7.08	3.03	3.27
February	2.25	15.68	5.70	3.48	3.00
March	3.24	14.37	11.56	9.29	8.03
April	2.66	26.97	24.84	5.87	3.80
May	1.99	23.11	6.78	4.23	2.39
June	2.10	16.79	8.91	3.75	3.05
July	5.13	23.68	23.55	20.42	19.64
Augus t	2.02	16.05	3.90	2.98	2.31
September	2.03	9.70	6.72	4.57	2.88
October	2.34	19.79	7.82	6.35	3.82
November	2.47	14.24	8.68	3.56	3.88
December	2.48	13.98	8.34	4.30	3.39
representa	tive yearly a	verage = 2.	58 ppmv		

		Table			
	Air Qua	lity Data fo	or CH4 in ppm	IV	
Monthlymax					
Month	Average	5-min	l-hr	3-hr	24-hr
January	2.37	10.03	7.49	2.75	2.79
February	2.44	8.87	5.29	3.62	2.82
March	2.28	8.50	5.21	3.85	2.76
April	2.04	25.42	17.68	6.04	2.29
May	1.96	14.03	4.40	3.82	2.41
June	1.93	14.35	7.38	3.62	2.79
July	2.61	7.91	7.58	6.34	6.51
August	1.90	8.39	3.74	2.52	2.26
September	1.84	6.34	4.68	3.24	2.60
October	2.11	13.99	6.63	4.71	3.07
November	2.12	10.52	5.43	3.08	3.08
December	2.36	11.98	7.45	4.08	3.21
representa	tive yearly a	verage = 2.	16 ppmv		

		Table			
	Air Qu	ality Data f	for RHC in pp	mv	
			C ma		
Month	Average	5-min	1-hr	3-hr	24-hr
January	0.06	4.30	2.62	0.25	0.16
February	0.04	13.45	1.51	0.36	0.27
March	1.02	8.37	6.38	5.82	5.36
April	0.95	24.98	11.29	1.81	1.51
May	0.12	20.93	4.67	1.89	0.40
June	0.28	14.19	3.00	0.72	0.52
July	2.53	16.06	15.97	7.55	
August	0.32	14.41	2.74		
September	0.26	7.05	2.14	1.69	0.72
October	0.32	15.70	3.42	1.48	0.74
November	0.44	7.93	3.57	0.88	0.88
December	0.23	6.37	1.77	0.87	0.70
representa	tive yearly a	verage = 0.	55 ppmv		

A common feature of the data in the tables is that, for any given month, the shortest time averaging period always has the highest concentration value, i.e., the 5-minute maximum concentration is higher in value than the 1-hour maximum concentration, etc. This concentration behavior is typical of all trace substances present in the ambient air. Conversely, the minimum concentration increases with longer time-averaging periods. These results are trivial because it should be expected that in a long sampling time, say, one month, there are more shorter time-averaging periods than longer time-averaging periods, so that the probability is higher for a 5-minute maximum concentration to have a larger value than the 1-hour maximum concentration. In other words, there are more concentration fluctuations with shorter time-averaging periods than longer time-averages. As longer time-averaging periods are used, concentration fluctuations tend to be damped.

Another common feature of the air quality data is that none of the gases have a normal, or Gaussian, concentration distribution in the atmosphere for a given time-averaging period. An analysis of all of the 1-hour data for each gas (see Table 1) has revealed that CO, NO, O_3 , RHC, and SO_2 follow a log-normal type distribution, while THC, CH_4 , and NO_2 have a more complicated concentration distribution.

For the 0_3 air quality data listed in Table 3, the most significant feature is the high concentration values during the warmer months for each of the time-averaging periods of interest. This is no coincidence since a prerequisite for 0_3 production is high air temperatures. An anamoly is the November data, but that month had unseasonably high temperatures.

For the SO_2 data listed in Table 4, the most significant feature is the generally higher concentration values during the colder months. This is to be expected since there is a higher demand on fuel and power requirements during the colder months.

For the NO data listed in Table 5, the most significant feature (even though the June and December Data are missing) is the generally higher concentrations during the colder months. Like SO_2 , NO is high in the colder months because of higher fuel and power use but, in addition, NO enters into less reactions during this period. In the warmer months, NO enters into the photochemical reaction scheme and, in addition, is an O_3 scavenger, entering into reactions with that pollutant and forming organic nitrogen compounds.

For the NO_2 data listed in Table 6, the most significant feature (even though the June and December data are missing) is that there is no apparent seasonal effect that can be detected with

certainty. Perhaps this is not too surprising since NO_2 is emitted in small amounts from all combustion sources, is a product of the oxidation of NO_1 , and is formed in the atmosphere; it is the single most important compound in the photochemical reaction scheme (8).

For the CO data listed in Table 7, the most significant feature is the generally higher values in the colder months. Some anomalies exist in the data because of the emission of this pollutant from random operations of nearby sources such as road and roof tarring operations and fire department training exercises (at Washington National Airport and from the District of Columbia Fire Department Training Facility). CO concentrations would also be expected to be lower in the warmer months because of its reactions with the hydroxyl radical (OH) (8,9). This free radical is very important in atmospheric chemistry, and would tend to be present in higher concentrations during the warmer months.

An interesting point about CO is that the quantity emitted, during a year, is equal to, or greater than the combined tonnage of all other air pollutants combined. Only carbon dioxide and water are emitted in greater amounts from combustion processes.

For the THC data listed in Table 8, there is no apparent seasonal effect. Because of the anomalous effect of random emission sources, such as those listed for CO, there were also occasions when solvent release occurred near the air sampling probe (intake). Specifically, painting operations, hood exhaust emissions, and solvent release from a newly constructed, slow-setting concrete facility, resulted in abnormally high THC concentrations.

For the CH4 data listed in Table 9, the most significant feature is that, for any given time-averaging period, the concentration values do not show much abnormal variations except for a few known types of anomalies. What is significant is that a major CH4 source exists near the Laboratory, i.e., the Blue Plains Sewage Treatment Plant. Fortunately, CH4 is not considered an air pollutant and its global background concentration of approximately 1.4 ppmv has not been found to be increasing. In addition, CH4 is not considered to be involved in any chemical reactions in the atmosphere, typical of paraffinic hydrocarbons, because of its low reaction rate with compounds involved in the photochemical reaction scheme. However, at long enough times, via long distance transport, CH4 may enter into chemical reactions with free radicals, notably the OH radical.

For the RHC data listed in Table 10, the significant feature is the generally higher concentration values in the warmer months. Generally, a large fraction of the hydrocarbons are emitted from combustion sources, but in a few instances, non-combustion sources, with minimal CH_4 emissions, are present in the NRL air environment so that RHC concentrations would tend to be high. Also, even with

combustion processes, the ratio of total hydrocarbons to methane is, in some cases, high so that, again, RHC concentrations are high. In addition, some organic compounds are formed in the atmosphere via the photochemical sequence of reactions which could also result in high RHC concentration values. However, it should be pointed out that not all RHC compounds are involved in photochemical reactions, i.e., their reaction rates are low. Consequently, they do not readily participate as precursors in oxidant formation.

In another approach to characterizing the air quality data, the 1-hour maximum concentrations that occurred, with the corresponding conditions of interest, are listed in Table II, for each air pollutant and gas, for each month of the year in which data were available.

Table 11 1-hr Maximum Concentration Values During Each Month of 1979 for Each Pollutant and Trace Gas and Corresponding Conditions

Air Temperature (^O C)	-10 12 16 27 28 31 28 12 12 12 12	-1.5 15 28 28 28 22 22 22
Relative Humidity (1)	30 42 42 33 47 47 45 39	90 79 79 74 74 74 75 74 74
Wind	S S S S S S S S S S S S S S S S S S S	NS NE E NE E SE
Wind Speed	15 0	7488999500 88
Hour of Day (Military Time)	1200 0500 1300 1500 1500 1500 1500	1800 1200 1200 1200 1400 0800 0800
Day	Wed Tue Fri Sun Wed Tue Tri Thu	Sun Sat Med The The Sat The Sat The Sat
Conc.	0.013 0.037 0.020 0.355 0.075 0.121 0.134 0.077	0.206 0.074 0.089 0.089 0.107 0.093 0.097 0.097
4	Jan Feb Mar Apr Jun Jun Sep Oct Nov	Jan Feb Mar Apr Jul Sep Oct Nov
	03	² 0s

Table 11
1-hr Maximum Concentration Values During Each Month of 1979
for Each Pollutant and Trace Gas and Corresponding Conditions

Air Temperature (⁰ C)	20 20 20 17 14	22 26 27 28 11 16
Relative Humidity (%)	28 27 28 28 29 29 20 20 20 20 20 20 20 20 20 20 20 20 20	85 72 88 89 15 15 15 15 15 15 15 15 15 15 15 15 15
Wind Direction	S SK NNE SK SK SK SK SK SK SK SK SK SK SK SK SK	SSE SW SW SW SW SW SW SW SW SW SW SW SW SW
Wind Speed (mph)	25 25 4 7 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	15 21 22 29 89 89
Hour of Day (Military Time)	2200 2300 2300 1200 0700 1800 2300 2200	2200 2300 2300 0400 0400 1500 1800 2300 2200
Day of Week	Wed Sat Sun Wed Wed Thu Thu Fri Sun	Wed Wed Sat Sun Wed The Thu Fri Mon Sun
Conc. (ppmv)	7.08 5.70 11.56 24.84 6.78 8.91 23.55 3.90 6.72 7.82 8.68	7.49 5.29 5.21 7.38 7.58 3.74 4.68 6.63 7.45
Month	Jan Feb Mar Jun Jun Sep Oct Nov	Jan May May Jul Nov Dec
Pollutant	THC	₽ .

Table 11
1-hr Maximum Concentration Values During Each Month of 1979
for Each Pollutant and Trace Gas and Corresponding Conditions

		
Air Temperature (⁰ C)	20 15 20 20 20 20 15	- 2 17 16 18 17 18 18 15
Relative Humidity (%)	7 - 2 88 - 2 83 - 2 100 - 1 69 - 1 83 - 1 84 - 1 84 - 1 85 - 1 85 - 1 86	61 36 36 73 100 75 48 48
Wind Direction	NNE NNE SSE SSE SSE SSE SSE SSE SSE SSE	E ENE NNE SSW NNE NNE NNE NNE NNE NNE
Wind Speed (mph)	88 102 103 103 104	10 10 10 10 10 10 10 10 10 10 10 10 10 1
Hour of Day (Military Time)	0700 1900 0500 0700 0700 1500 1000 2300 0600 0400	0700 0000 1200 1100 0800 0800 0700
Day of Week	Sat Sun The The Tue Sun Tue Tue	Tue Fri Sun Tue Tue Thu Med Med
Conc. (ppmv)	2.62 11.51 6.38 11.29 4.67 3.00 15.97 2.74 2.14 3.57	5.95 7.16 23.31 23.04 6.21 1.91 6.71 7.20 8.27 20.86 6.78
Month	May Mar May Jun Jun Sep Oct	Jan Mar May Jun Jul Sep Oct Dec
Pollutant	RHC	8

Table 11 1-hr Maximum Concentration Values During Each Month of 1979 for Each Pollutant and Trace Gas and Corresponding Conditions

Air Temperature (0C)	22 17 13 13 13 13 13	- 4 - 2 - 2 - 2 - 3 - 3 - 3 - 3 - 3 - 3 - 3 - 3 - 3 - 3
Relative Humidity (%)	97 100 100 100 100 100	88 88 89 100 100 100 100 100 100 100 100 100 10
Wind Direction	N N N N N N N N N N N N N N N N N N N	SSW NE NNE NNE NNE
Wind Speed (mph)	122 123 133 133 133 133 133 133 133 133	4 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
Hour of Day (Military Time)	2300 0300 0800 0700 0700 0700 0800 0900 0400	1600 0800 0700 2200 2200 1000 1000
Day of Week	Wed Fri Sat Fri Thu Wed Sun	Fri Thu Sat Sat Thu Wed Tue Thu Mon
Conc. (ppmv)	0.377 0.327 0.422 0.153 0.362 0.113 0.183 0.339 0.375	0.048 0.122 0.085 0.119 0.065 0.066 0.095 0.128
Month	Jan Feb Mar Jun Jun Sep Oct Dec	Jan Feb Mar Aur Jul Sep Oct Nov
Pollutant	ON.	NO ₂

For the 0_3 data in the table, the main characteristic feature is the occurrence of the maximum 1-hour concentrations in the afternoon hours; the highest values occurring in the warmer months with corresponding higher air temperatures. It is also noteworthy that these high concentrations occur with low wind speeds and relatively low relative humidity.

For the ${\rm SO}_2$ data in Table 11, the main characteristic is that maximum 1-hour concentrations occur from the westerly directions.

For the THC 1-hour maximum concentrations, the main characteristic is that the high concentrations occur in the late evening hours. In addition, another feature is that these high concentrations occur with southerly wind directions and from the NNE. Also, a number of the 1-hour maximum THC concentrations occur at high relative humidities. This suggests that a large fraction of the THC components might be water soluble.

For the CH_4 1-hour maximum concentrations listed in Table II, the main characteristics for these high values are that they occur during the early morning and late evening hours, with southerly wind directions, and at a high relative humidity.

For the RHC 1-hour maximum concentrations listed in Table 11, there do not appear to be any characteristic correlation with the corresponding conditions.

For the CO 1-hour maximum concentrations, the main characteristics are that these high values correspond to the mid-morning hours, northerly wind directions, and high relative humdities.

Any analysis of the data is retrospective in nature and reveals past and not future events. However, reasonable approximations to future behavior can be made based on past experience. For example, it was noted in the above analysis of the 1-hour maximum concentrations that some pollutants and gases had peak concentrations at certain times of the day. This is not fortuituous, but is the result of a combination of systematic variations of meteorological conditions and emission sources. Consequently, it seems reasonable to suspect that some of the pollutants and gases would follow a daily cycle. Emission sources, for example, might be expected to follow a daily routine of operations with some sources peaking at certain times of the day and/or with peak demands occurring with the season. In addition, meteorological conditions that follow a certain pattern include, night and day, higher air temperatures in the afternoon hours with corresponding increased sunlight intensity, higher relative humidities in the morning hours, and higher wind speeds in the afternoon. Obviously, there will be variations in these conditions, so

that if a definite pattern emerges for an air pollutant or gas it might be concluded that it follows a systematic variation in its daily cycle. Conversely, some air pollutants and gases may have no pattern so that irregular, or random variations occur during a day.

One way of depicting a daily profile is to plot on regular coordinate graph paper, a typical day's observations, i.e., the 1-hour average concentration against time of day. The problem with this method is in choosing a typical day as representative of all other days. Another way would be to average the concentrations of all the 1-hour averages, for a given hour, and plot the results against the time of day. This idea has merit and might be worth looking into at another time. A more elegant and simpler method is to determine, for a given day in which all 24 1-hour average concentrations are available, the time of day in which the highest 1-hour average concentration occurred. This would be done with all days in which data were available, the results tabulated, and the data plotted as the number of times the highest 1-hour average occurred at a given time of day. The results of the tabulations of the NRL air quality data, using this procedure, are shown in Figs. I-8 for 0_3 , NO, NO₂, CO, SO₂, THC, CH₄, and RHC, where the ordinate is the number of occurrences of the highest 1-hour average concentration occurring in a given day, and the abscissa is the time of day (00 is midnight, 12 is noon, and 23 is 11 p.m.).

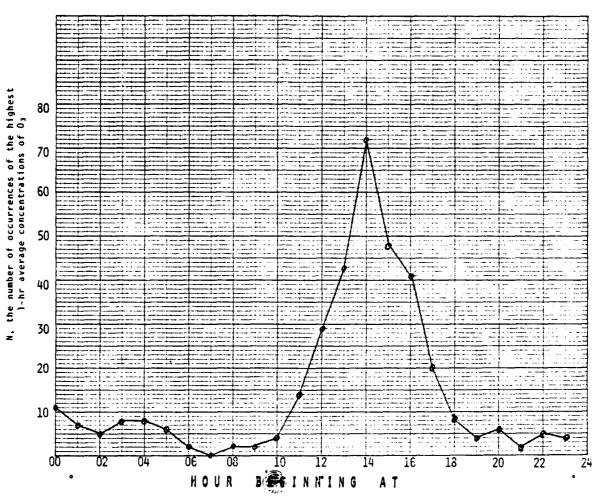


Fig. 1. - N, the number of occurrences of the highest 1-hr average concentrations of 0_3 of each day during 1979 as a function of the time of day.

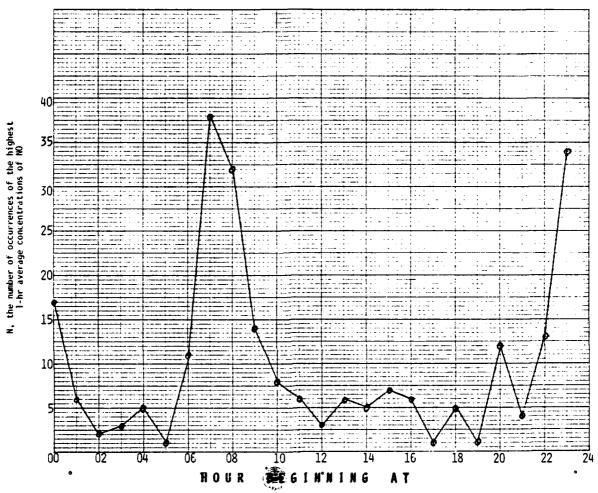


Fig. 2 - N, the number of occurrences of the highest 1-hr average concentrations of NO of each day during 1979 as a function of the time of day.

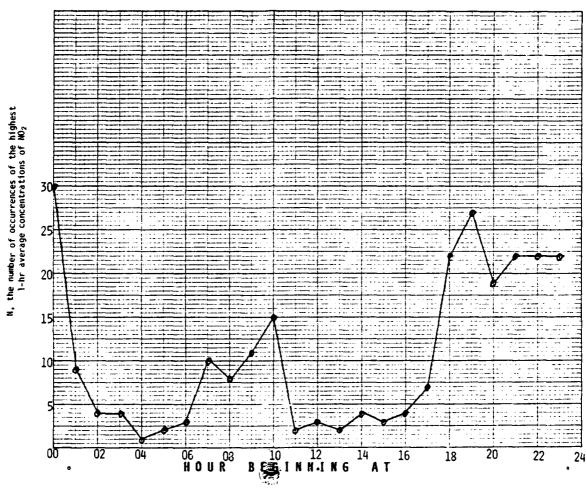


Fig. 3 - N, the number of occurrences of the highest 1-hr average concentrations of NO_2 of each day during 1979 as a function of the time of day.

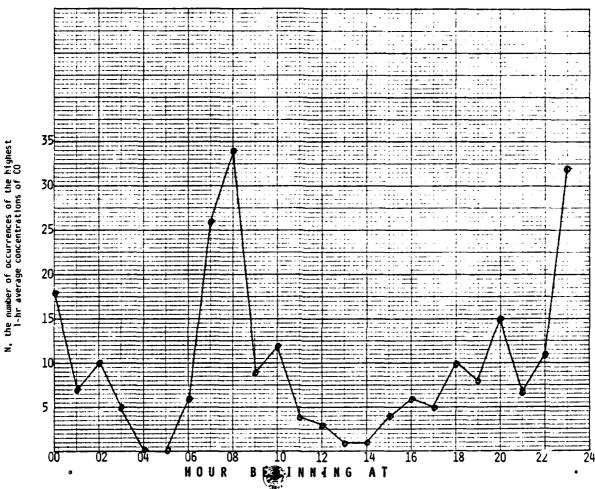


Fig. 4 - N, the number of occurrences of the highest 1-hr average concentrations of CO of each day during 1979 as a function of the time of day.

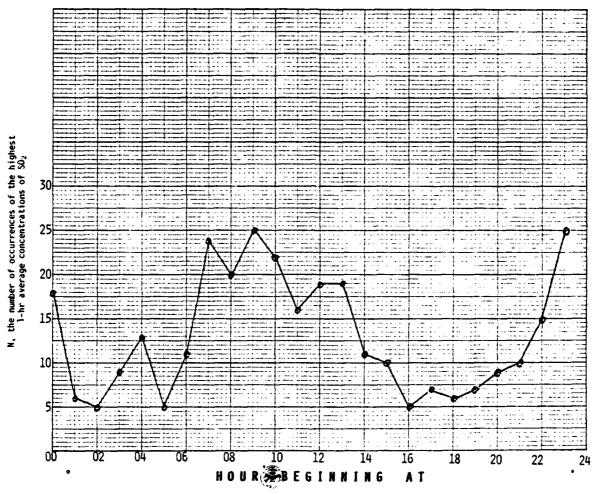


Fig. 5 - N, the number of occurrences of the highest 1-hr average concentration of SO₂ of each day during 1979 as a function of the time of day.

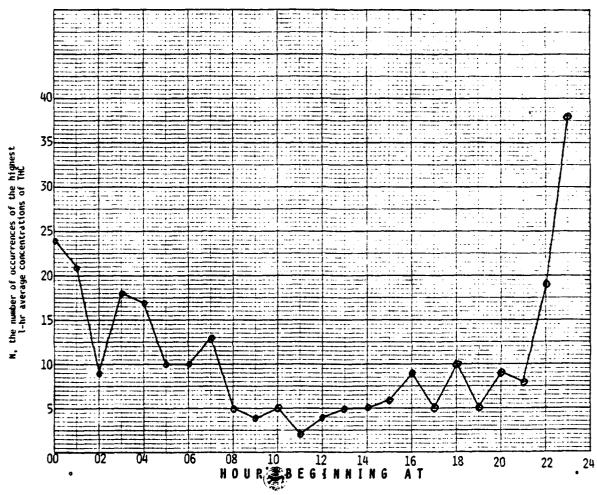


Fig. 6 - N, the number of occurrences of the highest 1-hr average concentration of THC during each day of 1979 as a function of the time of day.

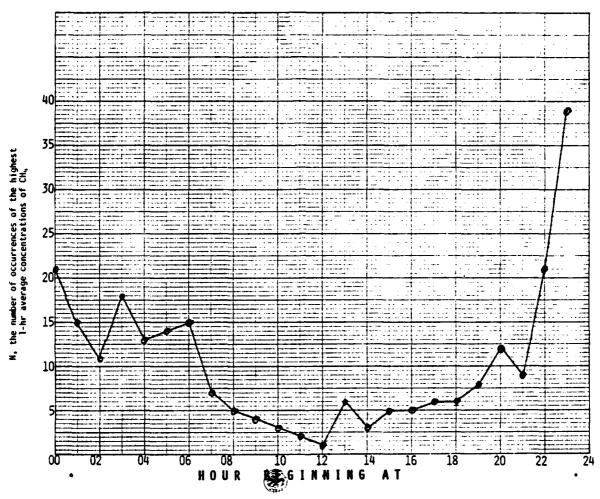


Fig. 7 - N, the number of occurrences of the highest 1-hr average concentrations of CH4 of each day during 1979 as a function of the time of day.

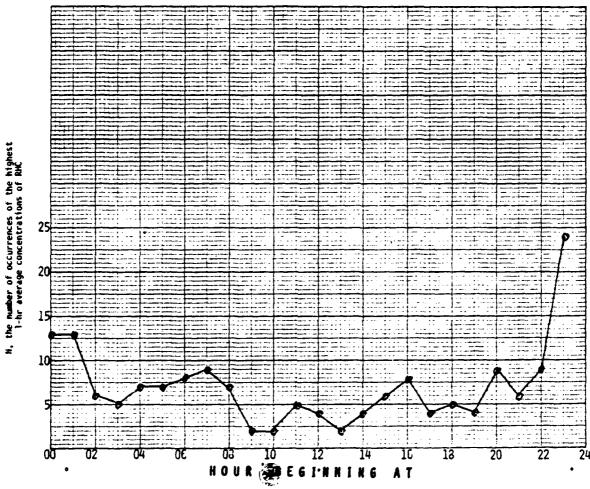


Fig. 8 - N, the number of occurrences of the highest 1-hr average concentrations of RHC of each day during 1979 as a function of the time of day.

Inspection of the figures reveals that there are, in a broad sense, three distinct characteristic daily profiles for the air pollutants and gases. One type is shown by 03 with a single peak occurring in the afternoon hours with the maximum at 2 p.m. Another characteristic profile is shown by NO, NO_2 , CO, and SO_2 , which have two daily peaks, one in the mid-morning hours and the other in the late evening and early morning hours. The third characteristic daily profile is shown by THC, CH_4 , and RHC, and is a U-shaped curve with the highest concentrations occurring in the late evening and early morning hours. The curves in the figures are not as smooth as might be desired, but this is a result of, and why they are called, systematic variations. Consequently, the single peak, double peak, and Ushaped daily profiles are examples of the pollutant concentration behavior to be expected of the air quality data. It should be emphasized that these curves pertain only to the NRL air quality data. However, similar shaped curves should be closely followed by the data collected at other air monitoring stations.

Other type curves that might be produced by other substances present in the atmosphere are: a daily curve with three or more peaks, and a daily curve with no peaks, i.e., a simple horizontal straight line. Examples of this curve would be the nitrogen and oxygen concentration data. These gases are the predominant and permanent gases present in the atmosphere. In any case, it is felt that any trace substance present in the atmosphere, and especially those emitted by human activity, or formed in the atmosphere by chemical reactions, will fall into one of three characteristic profiles shown by the NRL air quality data. This is an important conclusion because any change in the characteristic curve would mean a drastic change in meteorological conditions or in emission sources.

The chief disadvantage of the characteristic curves shown in Figs. 1-8 is that the concentration values are not given. However, work on the problem is continuing.

The 0_3 peak occurring during the afternoon hours, as shown in Fig. 1, is due to the favorable conditions for the formation during this period, i.e., sunlight, and the precursors RHC and $N0_2$. At other times of the day, maximum 0_3 concentrations are likely due to long distance transport of this pollutant from other metropolitan areas, or a tropospheric-stratospheric exchange. However, the highest 0_3 concentrations always occur in the afternoon hours. Lower concentrations at other times are due to the high reactivity of 0_3 with other substances.

The NO curve in Fig. 2 can be considered as a classic example of the double peak profile. It will be noted from inspection

of the figure that the mid-morning peak corresponds to the morning rush hour traffic period and to the human activities normally going on at this time. The combined late evening and early morning peak which occurs with NO, and all other gases with the exception of O₃, is not, as one might expect, associated with the evening rush hour traffic. The reasons for this peak are not clear but some possibilities are: long distance transport, bypass of pollution controls on certain combustion systems, concentration buildup in the surface-based temperature inversion layer, or a byproduct of chemical reactions occurring during this time period. These possibilities also apply to the other gases that have peaks in the late evening and early morning hours.

The double peak profile for NO_2 , as shown in Fig. 3, is not so smooth as that for NO, but is easily recognizable. It is fortunate that NO_2 does not have a single peak curve in the morning hours because this would ultimately result in higher 0_3 concentrations, or smog symptoms, than are now shown. Also, a comparison of Figs. 2 and 3 shows that the morning NO_2 peak occurs at a later time than the morning NO peak. This occurs because of the slow oxidation of NO to NO_2 , which takes time, and the reaction of NO with reactive hydrocarbons, with some NO_2 being formed. It should be pointed out, however, that NO_2 is also formed directly in high temperature combustion processes which use fossil fuels (coal, fuel oil, gasoline, natural gas). Normally, NO_2 has low concentrations during the afternoon hours, when 03 concentrations are high, because it is consumed in the photochemical reaction scheme to produce 03. As the sun goes down, the photochemical series of reactions ceases and the NO_2 concentration increases; this may be another reason for the late evening and early morning NO_2 peak (as shown in Fig. 3).

It is noteworthy that the CO double peak profile, shown in Fig. 4, closely resembles the NO_2 curve in Fig. 2. This is not fortuitous but suggests that the sources of these two gases are similar. Also, the morning CO peak corresponds to the morning rush hour traffic period as for NO. It is generally agreed that motor vehicle exhaust emissions are the principal source of CO in urban atmospheres. Other combustion sources also contribute to the CO in the atmosphere and their influence may be felt at other times of the day. This is a point worth re-emphasizing because at different times of the day different emission sources will, or might, bias the air quality data. It is also postulated that CO concentrations are lower in the afternoon hours because of reactions with the highly reactive hydroxyl free radical (OH). This free radical would tend to be lower in the nighttime hours and in the colder winter months. The hydroxyl radicals are formed by the reaction of water vapor with excited oxygen atoms, which, in turn, are formed by the photolysis of O_3 .

The double peak profile for SO_2 , shown in Fig. 5, is not as smooth a profile as one would like and could be subject to a different interpretation. However, the double peak profile for this pollutant is evident upon closer inspection of the curve. The first peak is extended from the morning to the early afternoon hours and covers a wide range of time. One reason for this is the close proximity of a coal-fired electric power plant, the NRL heating plant, and other nearby power plants. In the later afternoon hours, SO_2 concentrations are low because of the reaction of this pollutant with O_3 .

The U-shaped curves for THC, CH4, and RHC, as shown in Figs. 6, 7, and 8, respectively, are, in a general sense, closely alike. Note that the number of peak concentrations do not coincide with the morning and evening rush hour traffic periods. High concentrations do occur at these time periods but not as many times as in the late evening and early morning hours. Low concentrations of these gases, especially in the late morning and evening hours, suggest a good mixing of the gases in the atmosphere, a breakup of the surface-based temperature inversion layer with increased dilution, and dispersion, or a participation in the photochemical sequence of reactions.

AIR QUALITY STANDARDS

To protect human health and welfare, federal air quality standards have been issued for a number of air pollutants. The standards for those air pollutants measured at the NRL air monitoring station are listed in Table 12. The main change from previous years is the relaxation of the 0_3 standard from 0.08 ppmv to 0.12 ppmv. Included in the table is the number of times these standards have been exceeded at NRL. By the old 03 standard, this number would have been 112. In any case, this is not a bad showing for the NRL air environment if the air quality standards are used as a guide, but improvement in air quality is certainly required and constant vigilance is necessary. However, it should be remembered that the weather in 1979 was not as favorable for 03 formation as in other years. In fact, the possibility always exists that more favorable meteorological conditions, such as low relative humidity, strong sunlight, minimal cloud cover, and a stagnating high pressure system could trigger a sever air pollution episode and, especially, since the precursors for oxidant formation, reactive hydrocarbons, and nitrogen dioxide are always present in the atmosphere. It should also be remembered that lower concentrations of air pollutants may exert a subtle, or as yet unrecognized, effect on human health and welfare.

Table 12 National Ambient Air Quality Standards in ppmv and Times Exceeded				
				Times Exceeded at NRL
so ₂	0.03 (aam)*	•	primary	0
	0.14 (24-hr) 0.50 (3-hr)	-	primary secondary	0
CO	9 ppmv (8-hr) 35 ppmv (1-hr)	-	<pre>primary-secondary primary-secondary</pre>	
)) bbille (1 111)		primary secondary	
03	0.12 ppmv (1-hr)	-	primary	0
			secondary	12
RHC	0.24 ppmv (3-hr)	•	primary-secondary	70
NO ₂	0.05 ppmv (aam)*			0
annual ar	ithmetic mean		· · _ · · · · · · · · · · · · · ·	

ODOR NUISANCE AT NRL

One of the most immediate and recognized aspects of air pollution, besides the visibility degradation of the atmosphere, is odor pollution. Most people find, by common consent, that some odors, from specific facilities, are obnoxious and offensive. Odors from such facilities may cause headaches, nausea, vomiting, a general sense of discomfort, and a lowering of work performance. Other symptoms may appear such as loss of appetite, nervousness, and irritation of the eyes, nose, and throat. Some familiar examples of facilities that produce the odors that cause such symptoms are diesel buses and trucks, canneries, oil refineries, rendering plants, and sewage treatment plants. Each have their own characteristic emissions, but the common point is that these odors are a nuisance. Unfortunately, there are no odor pollution standards available to be enforced, so that the only recourse is by citizens' complaints and/or by use of public nuisance laws. In most cases, the subjective nature of the odor problem makes it difficult to enforce. Usually, one must appeal to the better nature of the offender in the spirit of fostering better community relations.

As yet, there is no fundamental theory of smell, and no basic odor detection device is available. No detector could come close to the odor detectability of the human nose with respect to extremely low concentrations, but some specific detectors have been developed for specific odorous sources. For example, hydrogen sulfide (H_2S) , a common odorous compound from sewage treatment plants, can easily be detected by some modern instrumentation.

Odor preception varies with the individual and will depend on age, environment, experience, health, race, and sex. It will also depend on the quality, strength, and the occurrence of the odor. Another possibility of odor perception is that one can be programmed to like or dislike certain smells. Most people have a normal sense of smell, but a few are odor-blind. There is another group of people who find all odors offensive, while others have only a partial sense of smell. In addition, some people have an exaggerated sense of smell and there is still another group whose sense of smell is stimulated by outside, non-odorous stimuli. Most people at the Laboratory will fall into one or more of these categories (10, 11).

Normal people can differentiate among several thousand odors, while an expert can differentiate several times that number. Usually, the compounds emitting these odors are organic in nature and in gaseous form. Solids and liquids, as such, do not emit odors. In addition, some odorous compounds are offensive at low concentrations and pleasant at higher concentrations, while for some other compounds the converse is true. In any case, odors range from pleasant to obnoxious and there is no good way to describe or classify them.

Odor perception is a part of everyday experience and starts at birth. As a consequence, every person lives in an odor-adapted environment. At times, this environment may be altered by the intrusion of foreign substances into the atmosphere, thereby creating an odor nuisance problem. Such intrusions occur at NRL. Because of the infrequent occurrences of these intrusions, there is not enough time for odor adaption to occur so that the smells are considered as offensive.

For the NRL air environment, these odorous intrusions are suspected to originate from the sewage treatment plant next door to the Laboratory. From this facility, odors are emitted from decomposing organic wastes, i.e., the bacterial breakdown products of fats and nitrogen and sulfur organic compounds (proteins). Consequently, odors are associated with sewage and sludge. The compounds from these wastes include organic acids, alcohols, aldehydes, amines, ammonia, carbon dioxide, carbon monoxide, hydrogen sulfide, mercaptans, methane, and sulfides. A combination of the odorous components is typical of sewage plant type odors. Usually, hydrogen sulfide is considered to be the compound most usually identified with sewage-type odors.

However, a mixture of various compounds results in the characteristic odor commonly identified with this type of facility. This odor has been described as cabbage-like, fecal, nauseating, obnoxious, offensive, rancid, or strong (12).

Odor control at the sewage plant is by chlorination treatment, a method that is usually effective. In addition, other measures, such as domed canopies, are used to contain odors. In any case, odor control is an expensive technology and only tried and true methods have been used. Consequently, any odors escaping from the facility must be considered as part of the "normal odor environment".

Finally, because of the ready identification of odors from the sewage plant, odors from other sources have been presumed to be due to this facility. These other sources have been found to be: painting opererations, solvent release from caulking materials used on the external parts of buildings, and solvent release from the slow-setting concrete formulations.

FUTURE PLANS

The work of the NRL air monitoring program will continue. In addition, a report will be published on a 5-year summary of the NRL air quality data collected from the years 1975-1979.

SUMMARY

The variables measured and recorded at the NRL air monitoring station include ozone (0_3) , sulfur dioxide $(S0_2)$, nitric oxide N0, nitrogen dioxide (NO_2) , total hydrocarbons (THC), methane (CH_4) , nonmethane hydrocarbons (RHC), carbon monoxide (CO), air temperature, relative humidity, wind direction, and wind speed. The air quality data analyzed from these variables is for the calendar year 1979. The main features in the report include representative yearly and monthly concentration averages, the maximum concentrations of various time-averages of interest, prevailing wind directions in decreasing order of percentage of occurrence, the number of times the federal air quality standards were exceeded, and trends and characteristics of pollutant behavior in the atmosphere. One of the main points in the report is that the pollutants and gases measured at NRL follow one or the other of three daily characteristic profiles: single peak, double peak, or U-shaped curves over the 24-hour period. In addition, a brief description of the odor nuisance problem at the Laboratory is described.

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